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STRUCTURAL INHOMOGENEITIES IN PYROCARBON COATINGS DEPOSITED IN THE FLUIDIZED BED

by

G. PELLEGRINI

1969

Joint Nuclear Research Center
Petten Establishment - Netherlands

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It turns out that the preferred orientation and the crystallite size increase continuously with the coating thickness, while the interlayer spacing decreases.

Emphasis is placed on measurements of the preferred orientation at various coating levels and on the precise X-ray technique and sample preparation necessary to achieve a reliable and reproducible measurement of this quantity.

A calculation of thermal expansion coefficients from the preferred orientation data shows that a difference of more than 15 % in thermal expansion exists between the innermost and outermost layers of the coating.

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ABSTRACT

An appreciable inhomogeneity in the structure of a 100 μ thick flat pyrocarbon coating deposited in a fluidized bed at constant temperature and gas composition has been found as a function of the thickness.

It turns out that the preferred orientation and the crystallite size increase continuously with the coating thickness, while the interlayer spacing decreases.

Emphasis is placed on measurements of the preferred orientation at various coating levels and on the precise X-ray technique and sample preparation necessary to achieve a reliable and reproducible measurement of this quantity.

A calculation of thermal expansion coefficients from the preferred orientation data shows that a difference of more than 15 % in thermal expansion exists between the innermost and outermost layers of the coating.

It is concluded that the differential strains which are generated by heating and under irradiation at high temperatures may seriously endanger the mechanical integrity of the coating.

KEYWORDS

PYROLYTIC CARBON
COATING
FLUIDIZED BED
ORIENTATION
X-RADIATION
EXPANSION
LAYERS
THICKNESS
STRAIN
HEATING
IRRADIATION

STRUCTURAL INHOMOGENEITIES IN PYROCARBON COATINGS DEPOSITED IN THE FLUIDIZED BED*)

1. Introduction

It is well known [1], that a rather large number of factors take part in forming the final structure of a pyrocarbon deposited in a fluidized bed. Some of them can be suitably chosen and controlled from the beginning of the coating process, such as the temperature and gas composition, the initial charge and the initial surface condition of the substrate, on which the pyrocarbon is deposited. Some others undergo continuous variations during the deposition, as e.g. the bed area, the bed volume, the state of fluidization, the rate of deposition per unit area, and the particle size which increases during deposition and which, therefore, affects factors not easily controlled during the coating operation. It is rather obscure up to this date, how seriously these intrinsic variations may affect the structural homogeneity of a coating.

Moreover, the reproducibility of a coating structure is still at present a subject of discussion. Discrepancies in structure have been encountered in samples obtained under analogous conditions in different coaters, as well as in samples of different charges coated in one and the same apparatus. But such structural deviations, which may arise from variations in the state of fluidization are not considered here. From some previous X-ray investigations, we observed that the most sensitive structural variations occur in individual coatings along the normal to the deposition surface. One may deduce that such inhomogeneities may become important in understanding some aspects of failure by irradiation at high temperature and they must be brought into consideration in any attempt at evaluation of structure-sensitive properties.

The main objective of the present investigation is to get qualitative and quantitative information about the structural inhomogeneities, which may appear in individual coatings throughout their thickness and/or in different samples of various dimensions taken from the same charge. For this purpose, the following structural parameters are considered: the mean interlayer spacing $\frac{\xi}{2}$, the mean crystallite size Lc and the preferred orientation, treated here in terms of Bacon Anisotropy Factor (B.A.F.)[2]

In order to learn the reliability of the preferred orientation measurements, the sensitivity and the reproducibility of the measuring method had to be proved first.

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*) Manuscript received on 25 March, 1969.

2. Experimental

2.1. Specimen preparation

To prepare the specimens used for the measurements, small discs of nuclear graphite were coated together with fuel particles in a fluidized bed. The discs are distinguished by the charge numbers WM 251, WM 253 and WM 252. The pyrocarbon deposit consisted of an inner coating of small thickness obtained at 1.700°C from C_2H_2 and in a more dense outer coating deposited from CH_4 at 2050°C. Only the outer coating has been used for the present investigations. A more complete description of the deposition data relative to the outer coatings is given in table 1.

TABLE 1

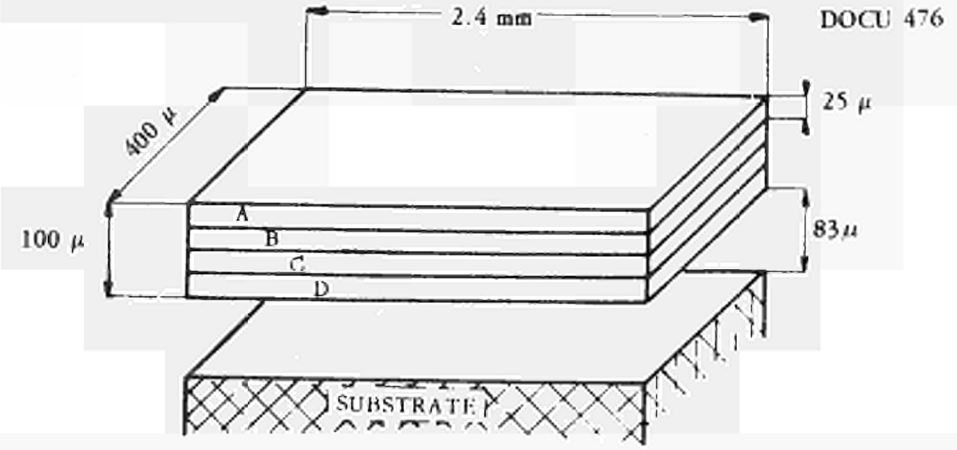
Charge	Gas comp.	Total pressure	Temp.°C	Initial surface area	Avg. Depos. rate	Average Density	Thick-ness
WM 251 outer coating	CH_4 76.2% + Argon	250 Torr	2050°	2.1 m^2	61 µ/h	2.05g/cm^3	57µ
WM 253 outer coating	CH_4 56.4% + Argon	200-250 Torr	2050°	0.93 m^2	38 µ/h	2.03g/cm^3	183 µ
WM 252 outer coating	CH_4 72.2% + Argon	250-400 Torr	2050°	2.15 m^2	47 µ/h	2.03g/cm^3	90 µ

Coating conditions of the samples used in the present investigation. All runs were carried out in a coater of 80 mm diameter.

From the charge WM 251 five discs of different diameters, resp. of 2.4, 3.8, 6, 8 and 10 mm have been chosen for the X-ray measurements. Each disc has been cut into two or more small strips of 2.4 mm length, 0.4 mm breadth and about 50 - 60 u thickness. This rather laborious specimen preparation procedure enables more measurements on the same coating and a standardization of the measuring method in order to minimize the experimental error.

For the investigation of possible inhomogeneities throughout the coating thickness, a disc of 10 mm diameter of the charge WM 253 was cut in the same way. The original coating thickness (183 µ) has been first reduced to 100 µ by simply

grinding the inner surface on a polishing machine. Afterwards four sets of samples of 2.4 mm length, 0.4 mm width and 25 μ thickness have been prepared, each set representing a different coating level with respect to the substrate. A sketch of the cutting practice is shown below:



In order to get some information about the influence of the substrate on the resulting structure of the coating, samples of the charge WM 252 have been used. Some of these samples were introduced into the bed later on without inner coating in order to reproduce the final coating stage on a non-oriented substrate. The surface area of the samples so introduced, ca. 0.01 m^2, was negligible in comparison with the total area already present (table 1). The anisotropy of the coating obtained in this way is compared to that of the upper part of the coatings, which were present in the bed from the beginning of the coating cycle.

2.2. X-ray methods

2.2.1. Measurement of the mean interlayer spacing $\frac{\bar{c}}{2}$

Debye-Scherrer photographs have been taken from the strip-shaped small specimens using a 114.6 mm camera and filtered $Cu_{K\alpha}$-radiation. The specimens were rotated during exposure.

The spacings $\frac{\bar{c}}{2}$ have been evaluated from the line position of the (002) and (004) reflections according to the well-known Bragg relationship:

$$\lambda = 2d \sin\vartheta \qquad (1)$$

where ϑ is the glancing angle and λ the wavelength of the CuK_α radiation.

During each measurement, care has been taken to maintain exactly the same experimental conditions.

2.2.2. Measurements of the apparent crystallite size Lc

The crystallite size Lc has been evaluated from the (002) line width at half maximum using the simple relationship

$$Lc = \frac{\lambda \cdot K}{B \cos \vartheta} \qquad (2)$$

where B is the line width at half peak height in radians and K = 0,89 is the Scherrer constant valid for turbostratic carbons [3]. Before measuring the line width, the Lorentz-polarization correction has been applied.

2.2.3. Measurements of the preferred orientation

The preferred orientation has been expressed in terms of Bacon anisotropy factors (hereafter referred to as B.A.F.), which represent the theoretical ratio of the thermal expansion coefficients of a coating normal and parallel to the deposition plane at 400°C [2]. The technique employed was the photographic Bacon technique as modified and refined by Bokros [4]. The experimental arrangement for CuK$_\alpha$ radiation is shown in fig. 1.

The specimen is mounted on a goniometer head and oriented in such a way, that the (002) diffraction ring is recorded on the film. The integrated intensity of the (002) diffraction peak at any angular position γ around the diffraction ring, after correction for absorption, is proportional to the number of crystallites oriented for diffraction in that direction. The angle γ measured on the film is related to the angle between the (002) pole of the diffracting crystallites and the normal to the deposition plane φ by:

$$\cos\varphi = \cos^2 77^\circ - \sin^2 77^\circ \cdot \sin\gamma \qquad (3)$$

The blackening on the top of the ring (γ = -90) is thus produced by the crystallites, whose (002) diffracting planes are parallel to the deposition surface, while the blackening at the right corresponds to the (002) crystallite planes lying normal to the surface of deposition.

The intensity of blackening of the photographic film across the diffraction ring has been measured in steps of 4° γ in the range between -90° to 0° γ

The absorption correction of the reflected intensities at various values of γ has been applied using the corresponding absorption curves calculated by Bokros for samples with known density and well-defined dimensions [4].

3. Results

3.1. Sensitivity of the method for measuring the anisotropy

Two samples of the charge WM 253, namely A and D of the sketch illustrated in page (4) have been measured twice, taking care that the exposure time and the film type were the same for each measurement. The anisotropy values obtained were,

for A: $1,74_2$ and for D: $1,28_7$
$1,72_6$ $1,28_4$

Measurements made on three different samples, all taken from one disc of the charge WM 251 furnished following values:

$1,36_4$
$1,36_4$
$1,41_1$

The thickness of the specimens were 60 μ, 60 μ and 55 μ resp.

Since care has been taken in using exactly the same experimental arrangement for each measurement, it is estimated that the error in B.A.F. is less than 5%. This level of error may be increased, to a small degree, by such problems, as inadequate film exposure or use of sample geometry, for which the absorption corrections are not well-defined.

3.2. Structural inhomogeneities throughout the thickness of the coating

The measurements of interlayer spacing $\frac{\bar{c}}{2}$, crystallite size Lc and Bacon anisotropy B.A.F. on sample WM 253 at different coating levels from the initial deposition surface led to the results, which are given in table 2

TABLE 2

coating sections	Mean distance from the substrate	$\frac{\bar{c}}{2}$ Å	Lc Å	B.A.F.
A	165 μ	*$3.42_2 \pm 0,005$	90 ± 10%	1,73 Error: less than 5%
B	145 μ	3.42_5	84	1,54
C	120 μ	3.42_9	75	1,35
D	95 μ	3.43_1	75	1,28

WM 253 interlayer spacing $\frac{\bar{c}}{2}$, crystallite size Lc and Bacon anisotropy factor B.A.F. as obtained for different coating levels with respect to substrate.

* Each value is the average of two measurements made on strips taken from the same level.

The results are illustrated in Fig. 2 and Fig. 3 in which the experimental values are plotted against the mean distance from the initial deposition surface.

One notes a continuous increase of the preferred orientation in the direction away from the substrate, the anisotropy factor of the outermost layers being about 40% greater than that obtained for the layers adjacent to the substrate. At the same time a slight improvement of the crystallinity of the deposit is observed in the same direction.

The specimen added to the charge WM 252 toward the end of the coating cycle yielded an anisotropy factor of 1.25. This value is somewhat smaller than that obtained from the upper part of the coatings, which were kept in the bed from the beginning of the coating process (B.A.F. = 1.32)

3.3. Investigation of the structural homogeneity in different coatings of the same charge

Five discs of resp. 2.4, 3.8, 6, 8 and 10 mm diameter belonging to the charge WM 251 have been used for measuring the Bacon anisotropy. The specimens were prepared in the way already described in section 2.1. The anisotropy values obtained are reported in table 3.

TABLE 3

Diameter	Specimen thickness	B.A.F.
*10 mm 1)	60 u	1.36 ± 0.05
2)	60 u	1.36
3)	55 u	1.41
8 mm	60 u	1.44
6 mm	50 u	1.37
3.8 mm	50 u	1.40
2.4 mm	50 u	1.36

Bacon anisotropy factors as obtained from discs of different diamater coated at 2050°C from 76,2% CH_4

Taking the experimental error into account, one can observe that there is no evidence of appreciable inhomogeneity in the Bacon anisotropy factor between different samples of the same charge, nor in a single sample as far as the same coating level is considered. Moreover, it can be seen that, in a diameter range up to 10 mm, the original dimensions of the particles used as substrate, do not affect the resulting structure of the coating.

* Three strips of 2.4mm length and 0.4mm width were prepared from this disc

3.4. Mean anisotropy factor

Considering the results of the measurements made on the coating levels A, B, C and D of the sample WM 253, it is evident that a mean value of a given structural property is obtained, if a relatively thick specimen is used. The anisotrpy factor obtained from a 100 μ thick specimen of the same charge was 1.35, while the arithmetical mean obtained by averaging the anisotropy factors of the single coating levels A, B, C and D is 1.47.

This may indicate that measurement made on thick samples may give anisotropy values which are somewhat too small.

Mean anisotropy factors relative to the samples of the charges WM 251, WM 252 and WM 253 and valid for a coating thickness of 60 μ, 75 μ and 100 μ resp. are summarized in table 4.

TABLE 4

Charge	Measured thickness	mean B.A.F.
WM 251	60 μ	1.37
WM 252	75 μ	1.25
WM 253	100 μ	1.35

Mean anisotropy factors as obtained from the coatings WM 251, WM 252 and WM 253 with a thickness of resp. 60, 75 and 100 u.

It is obvious that an attempt to interpret these values on the basis of the coating variables (e.g. coating rate) given in table 1, is a somewhat hazardous procedure, as far as not the same coating thickness is considered.

4. Discussion of the results

4.1. Increase in crystallinity and preferred orientation during deposition.

It must be noted that an attempt to explain the increase in crystallinity and preferred orientation during deposition is somewhat speculative, insofar as the knowledge about the differential effects affecting the state of fluidization is rather incomplete up to this date. Nevertheless, an interpretation may be given on the basis of the bed area , whose value increases continuously during deposition.

Experiments carried out by Bokros [1] and Grisdale [5] show that the coating efficiency (= ratio between the total carbon deposited and the total carbon introduced as gas into the coater), is independent of bed area, except for very low methane concentrations.

The rate of increase in diameter of a particle during deposition is then inversely proportional to the bed surface area, i.e. inversely proportional to the square of the diameter of the particle. This means that, after deposition of a 100 u thick coating on a particle having an original radius of the same magnitude, the coating rate (μ/h) is four times slower than it was at the beginning of the coating cycle, providing that the original coating variables have been kept constant.

Assuming that the discs used in the present investigations are representative for spherical particles of small diameter the variation of the anisotropy with the coating level may be approximated by:

$$\frac{B.A.F.}{B.A.F._o} = e^{0,25\left[\left(\frac{r}{r_o}\right)^2 - 1\right]} \qquad (4)$$

where $B.A.F._o$ and r_o are resp. the Bacon anisotropy and the particle radius at the beginning of the coating cycle.

The value $B.A.F._o$ is obviously depending on the choice of the coating parameters, e.g. bed temperature, gas composition, nature of the substrate and initial surface area of the bed. Since $\left(\frac{r}{r_o}\right)^2 = \frac{\mu_o}{\mu}$ (where μ_o and μ are the coating rates when the particles have resp. the radius r_o and r), the equation 1) may be written:

$$\frac{B.A.F.}{B.A.F._o} = e^{0,25\left(\frac{\mu_o}{\mu} - 1\right)} \qquad (5)$$

This expression is graphically represented in Fig. 4

According to the observations of Bokros [1] and Grisdale et al.[5] the pyrocarbon is formed by direct condensation on the surface of the bed of high-molecular-weight planar molecules, which have already been produced in the gas phase. The amount and the size of such molecules formed per unit time in the gas phase depend on the temperature and hydrocarbon concentration. The larger the planar complexes formed in the gas phase and the slower the condensation on the surface, the greater the probability for an effective alignment with each other and with the deposition plane. But also a certain amount of poorly ordered carbon matter (amorphous carbon and misaligned layers) is deposited at the same time and incorporated into the deposit. From the analysis of the scattering curve at low angles [6] this amount may vary from a few per cent for coatings obtained at high temperatures and low methane concentrations up to 15% for deposits manufactured at low temperatures, high methane concentrations and high deposition rates.

The surface mobility being high at a deposition temperature of 2000°C, a rearrangement of the freshly deposited carbon films may be expected to occur. The rearrangement is expected to be facilitated by low exposition rates and by a substrate which is already somewhat oriented.

In a study of the graphitization of carbon black, B.E.Warren [7] found that the graphitization process becomes evident mainly at temperatures around 2000°C. Ordering of the nearest-neighbour layers occurs at this temperature, resulting in an appreciable decrease in the average layer spacing, in a sharpening of the (00ℓ) peaks and in the appearance of the two-dimensional (hk) reflections. These observations are in agreement with our results obtained from a coating before and after heat treatment at 2000°C (Fig.5)

5. Effect of the anisotropic inhomogeneities on the bulk thermal expansion of a flat coating and its behaviour at high temperatures.

5.1. Approximation of the orientation function $1(\varphi)$

For some purposes, e.g. the evaluation of the bulk thermal expansion, it is useful to describe the experimental intensity distribution curve $1(\varphi)$ by a well-defined numerical relationship. Some authors [8, 9] use the approximation $1(\varphi) \approx \cos^n\varphi$ and consider the arbitrary parameter n as an indicative measure of the anisotropy. This approximation, however, is limited by the assumption that the reflected intensity becomes 0 at a given value of φ. That is not the case for very low anisotropies, where there is always a certain amount of reflection, even at $\varphi = 90^\circ$.

In describing the intensity distribution curves as obtained from the coating sections A, B, C, D, the approximation

$$1(\varphi)_{normalized} = a(\cos^n\varphi - 1) + 1 \qquad (6)$$

has been used here, where n is an arbitrary parameter and a is related to the normalized scattered intensity b at $90^\circ\varphi$ by

$$b = 1-a \qquad (7)$$

The a- and n-values provided by the computer for the consecutive coating sections are given, together with the corresponding B.A.F. values, in table 5.

TABLE 5

Coating section	a	n	B.A.F.
A	0,74 ± 0,006	2,62 ± 0,02	1,73
B	0,54 ± 0,02	4,13 ± 0,07	1,54
C	0,42 ± 0,02	5,34 ± 0,08	1,35
D	0,66 ± 0,01	0,53 ± 0,02	1,28

Constants (a,n) as obtained from the approximation of the normalized intensity distribution curve by $1\varphi) = a(\cos^n\varphi - 1)+1$

Fig. 6 shows the normalized intensity distribution curves of coating sections A, B, C and D as measured and as calculated by means of equation 6. It can be seen, that a quite good agreement between the two curves exists, for the case of the two extreme coating sections A and D.

5. 2 Evaluation of the bulk thermal expansion coefficients $a_{\parallel}$ and $a_{\perp}$

According to G.E. Bacon [2] the thermal expansion of a polycrystalline aggregate may be described in terms of orientation of the individual crystallites. For a layered structure such as pyrocarbon, the expansion coefficients parallel and perpendicular to the layer planes may be written:

$$a_{\parallel} = \alpha_a + \frac{\alpha_c - \alpha_a}{2} \cdot \frac{\int_0^{\frac{\pi}{2}} I(\phi) \sin^3\phi \, d\phi}{\int_0^{\frac{\pi}{2}} I(\phi) \sin\phi \, d\phi} \tag{8}$$

$$a_{\perp} = \frac{\alpha_c \cdot \int_0^{\frac{\pi}{2}} I(\phi) \cos^2\phi \sin\phi \, d\phi + \alpha_a \int_0^{\frac{\pi}{2}} I(\phi) \sin^3\phi \, d\phi}{\int_0^{\frac{\pi}{2}} I(\phi) \sin\phi \, d\phi} \tag{9}$$

where αa and αc are the lattice expansion coefficients along the a- and c-axis respectively; φ is the angle between the basal plane normal and the normal to the deposition plane. The intensity $I(\varphi)$ is proportional to the number of crystallite axes per unit solid angle lying at an angle φ.

Substituting $I(\varphi)$ in equations 8) and 9) by equation 6) and integrating one obtains:

$$a_{\parallel} = \alpha_a + \frac{\alpha_c - \alpha_a}{2} \cdot \frac{6a + 2(n+1)(n+3)(1-a)}{3(n+3)[a+(1-a)(n+1)]} \tag{10}$$

$$a_{\perp} = \frac{\alpha_c \cdot ((n+1)[3a+(1-a)(n+3)]) + \alpha_a \cdot [6a+2(n+1)(n+3)(1-a)]}{3(n+3) \cdot [a+(1-a)(n-1)]} \tag{11}$$

Using the lattice thermal expansion coefficients α_a and α_c measured by Nelson and Riley [10] on a Ceylon graphite and our calculated a- and n-values, the bulk expansion coefficients parallel and perpendicular to the deposition plane have been derived for the coating sections A and D, for which the approximation [6] holds very well.

The results thus obtained for 400°C and 800°C are shown in the following table.

TABLE 6

	400°C			800°C		
	$\alpha_a = 0\,(10)$ $\alpha_c = 28{,}3\times10^{-6}\,(10)$			$\alpha_a = 0{,}9\times10^{-6}\,(10)$ $\alpha_c = 28{,}3\times10^{-6}\,(10)$		
coating section	$a_{\parallel}$	$a_{\perp}$	$a_{\perp}/a_{\parallel}$	$a_{\parallel}$	$a_{\perp}$	$a_{\perp}/a_{\parallel}$
A	$7{,}50\times10^{-6}$	$13{,}30\times10^{-6}$	1,77	$8{,}14\times10^{-6}$	$13{,}77\times10^{-6}$	1,69
D	$8{,}63\times10^{-6}$	$10{,}75\times10^{-6}$	1,24	$9{,}25\times10^{-6}$	$11{,}29\times10^{-6}$	1,22

Bulk thermal expansion coefficients parallel and perpendicular to the deposition plane at 400°C and 800°C as calculated for coating section A and D with a B.A.F. of resp. 1,73 and 1,28*

One observes that, in a direction parallel to the substrate, the levels close to the surface of the deposit are subjected to a thermal expansion which is sensibly smaller than that of the levels lying directly above the substrate. On the contrary, the thermal expansion of these levels perpendicularly to the deposition plane is much less than that of the levels lying directly above the substrate.

5.3. Deformation of coatings by heat treatment and by irradiation at high temperature

Measurements of the preferred orientation carried out by R.H. Knibbs and I.B. Mason [8] on pyrolytic graphite samples prepared at 2150° and subsequently heat treated for ½ hour at 2700° and 2900°C show that a continuous improvement of the crystallite alignment occurs.

Moreover, it has been observed elsewhere [11] that the improvement of the crystallite alignment is accompanied by a decrease of the interlayer spacing and an increase of the crystallite size as far as the temperature of heat treatment lies around or above the deposition temperature of the pyrocarbon.

* The values reported above do not account for accomodation effects. Moreover, the use of the lattice thermal expansion coefficients of a natural graphite single crystal in evaluating the bulk thermal expansion implies the conception of a pyrocarbon consisting of an aggregate of well-defined crystallites.

In order to prove the above, the interlayer spacing, the crystallite size and the Bacon anisotropy factor have been measured on a coating deposited at 2000°C, before and after heating for 8 hours at 2000°C. The results are shown in Table 7. The scattering diagrams obtained from this sample before and after heat treatment are shown in Fig. 5a and 5b.

TABLE 7

Before heat treatment			After heat treatment		
$\frac{\bar{c}}{2}$ Å	L_c Å	B.A.F.	$\frac{\bar{c}}{2}$ Å	L_c Å	B.A.F.
3.430	137	1.20	3.419	172	1.61

Mean interlayer spacing $\frac{\bar{c}}{2}$ crystallite size Lc and Bacon anisotropy factor B.A.F. of a coating deposited at 2000°C, as measured before and after heating for 8 hours at 2000°C.

Taking the model of Jenkins and Williamson (12) for describing the stress-strain relationship in graphite by thermal cycling into account, one may deduce, that the difference in thermal expansion parallel to the deposition plane between the surface layers and those close to the substrate, produces a thermal stress, which is proportional to $(a_{\parallel D} - a_{\parallel A})$. ΔT, where $a_{\parallel D}$ and $a_{\parallel A}$ are the expansion coefficients of the inner and outer layers respectively, and ΔT the temperature difference in the thermal cycle.

One may assume that these differential thermal strains favour a "dewrinkling" of the original wrinkled sheet structure at high temperature [13] which, in turn, facilitates some other processes as i.e. plastic flow and structural rearrangements, such as increase in crystallinity and preferred orientation. All these effects may finally result in a permanent deformation of the coating after heat treatment.

The above assumption was investigated by heating several coatings, which were previously removed from the substrate by means of a lathe and marked on the upper surface, in a high frequency furnace for 8 hours at 2000°C. Subsequently, they were cooled down by simply switching off the furnace power. The estimated temperature fall was about 1500°C in 20 seconds. The photographs of the coatings treated in this way are given in figs. 7 and 8. It was observed that the bending appearing on the photographs became accentuated on repetition of the heat treatment.

These differential strain effects may also be expected to appear in discs placed under fast-neutron irradiation. A graphite crystal under fast neutron bombardment expands in the direction normal to the basal plane, while the basal plane contracts. That fact is discussed by Kelly et al.[14] in terms of nucleation of planar clusters of interstitial atoms and of collapse of vacancy lines due to atomic displacements. Measurements of dimensional changes made on pyrocarbon discs after irradiation up to 1200°C [15, 16] show that the shrinkage occurring parallel to the disc plane increases with the temperature and dose of irradiation. Taking the model of Kelly et al. [14] into account, one may deduce that, in an inhomogeneous coating, the layers with a higher degree of preferred orientation contract more than those with a lower degree of preferred orientation. The combined effect of the thermal and irradiation stresses may result in a strong bending of the coating accompanied by the formation of a number of large fractures across the basal planes.

This type of behaviour has been observed with various discs irradiated at 1250°C with a fluence of $6.3 \times 10^{21} n/cm^2$ [17].

6. Conclusions

Measurements of the Bacon anisotropy factor, of the crystallite size Lc and of the interlayer spacing $\frac{c}{2}$ at different deposition levels of a 100µ thick coating show that the structural properties vary continuously with the coating thickness.

An appreciable increase of the anisotropy , accompanied by a slight improvement of the crystallinity of the deposit from the substrate toward the surface has been found. This corresponds to a progressive decrease of the deposition rate per unit area as a consequence of the total bed volume increase. That is in agreement with the assumption that the pyrocarbon is formed by direct condensation on the surface of the bed of rather large planar molecules, which are already produced in the gas phase. The slower the condensation on the substrate and the better the orientation of the surface films, the greater the probability for a more perfect alignment with the deposition surface.

From consideration of the anisotropic dimensional changes during heat treatment and during irradiation at high temperatures, it has been deduced that a gradient of anisotropy throughout the coating thickness may seriously endanger the mechanical integrity of the coating.

An investigation of the possible inhomogeneities at different points of the coating section parallel to the deposition plane did not reveal appreciable structural differences. Such differences are not even observed in different samples from the same single coating charge.

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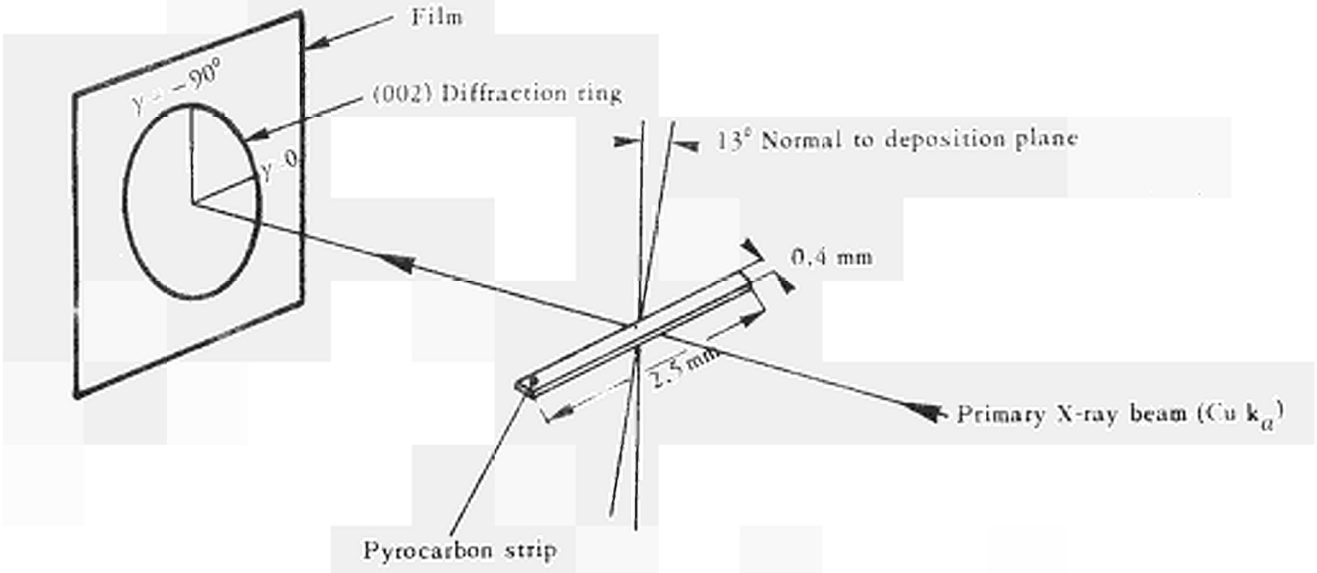
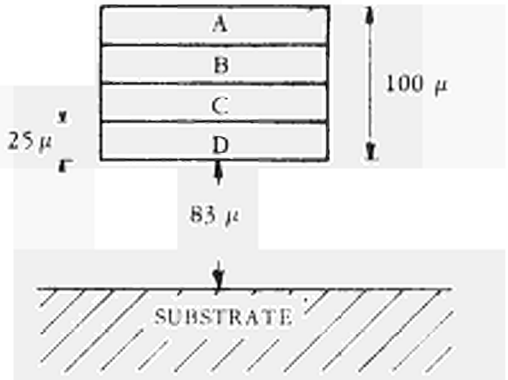


Fig. 1 Experimental arrangement for the measurements of the preferred orientation.



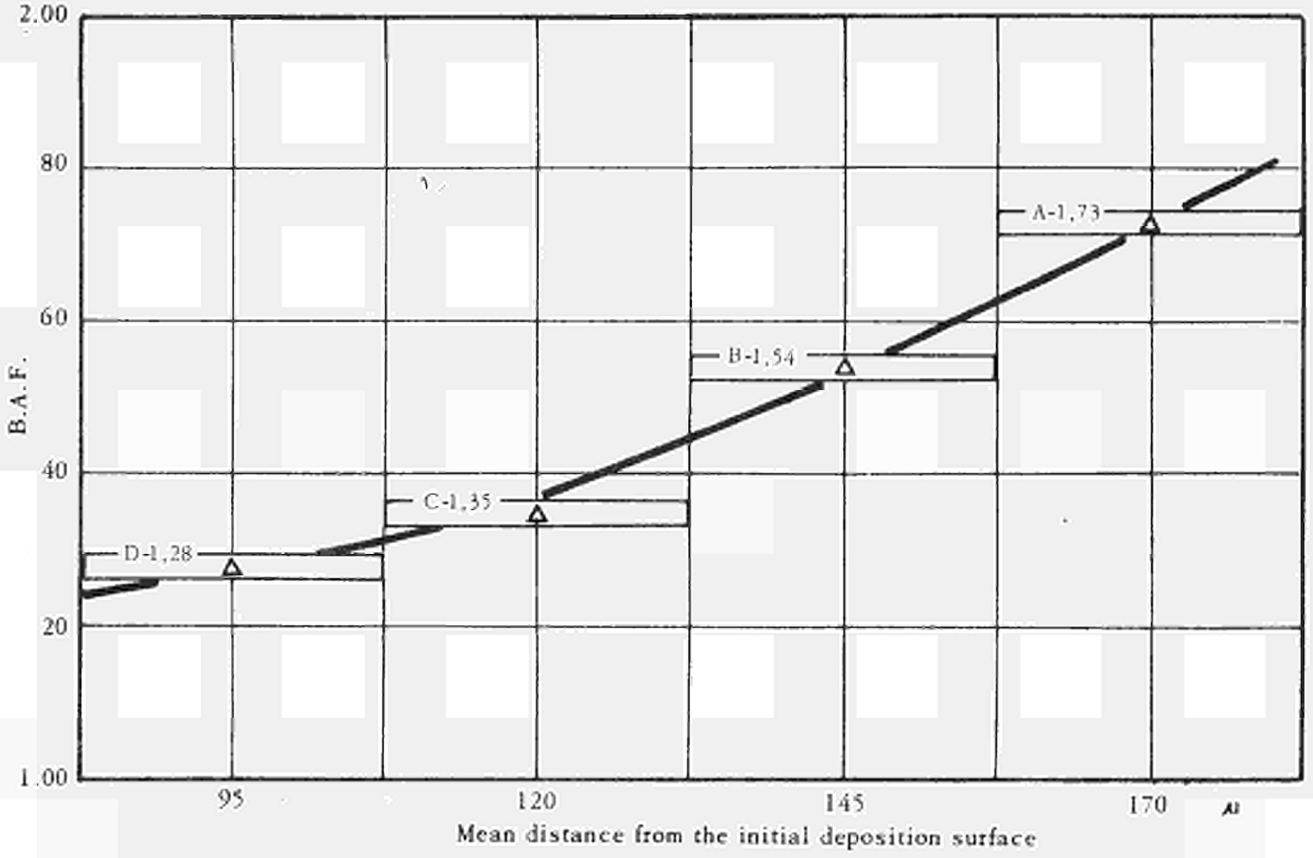
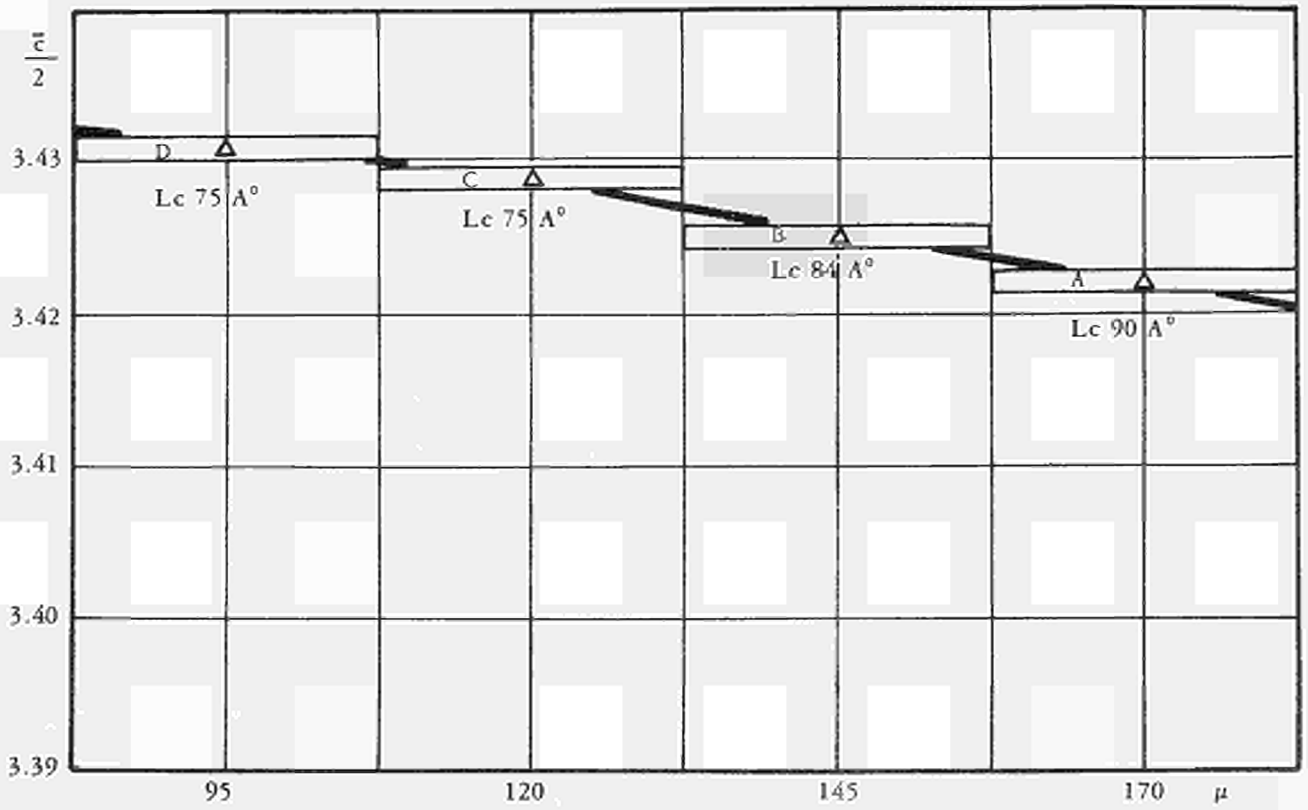


Fig. 2 WM 253 Bacon anisotropy factors as determined in successive coating sections parallel to the deposition plane.



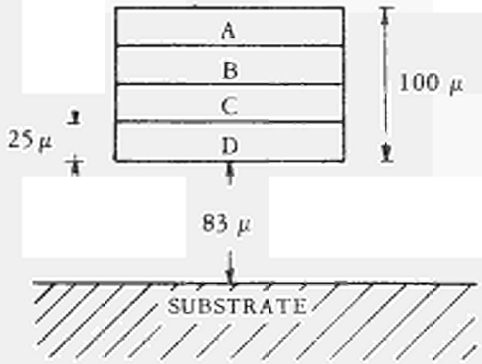


Fig. 3 WM 253, $\frac{c}{2}$ and Lc as determined in successive coating sections parallel to the deposition plane.

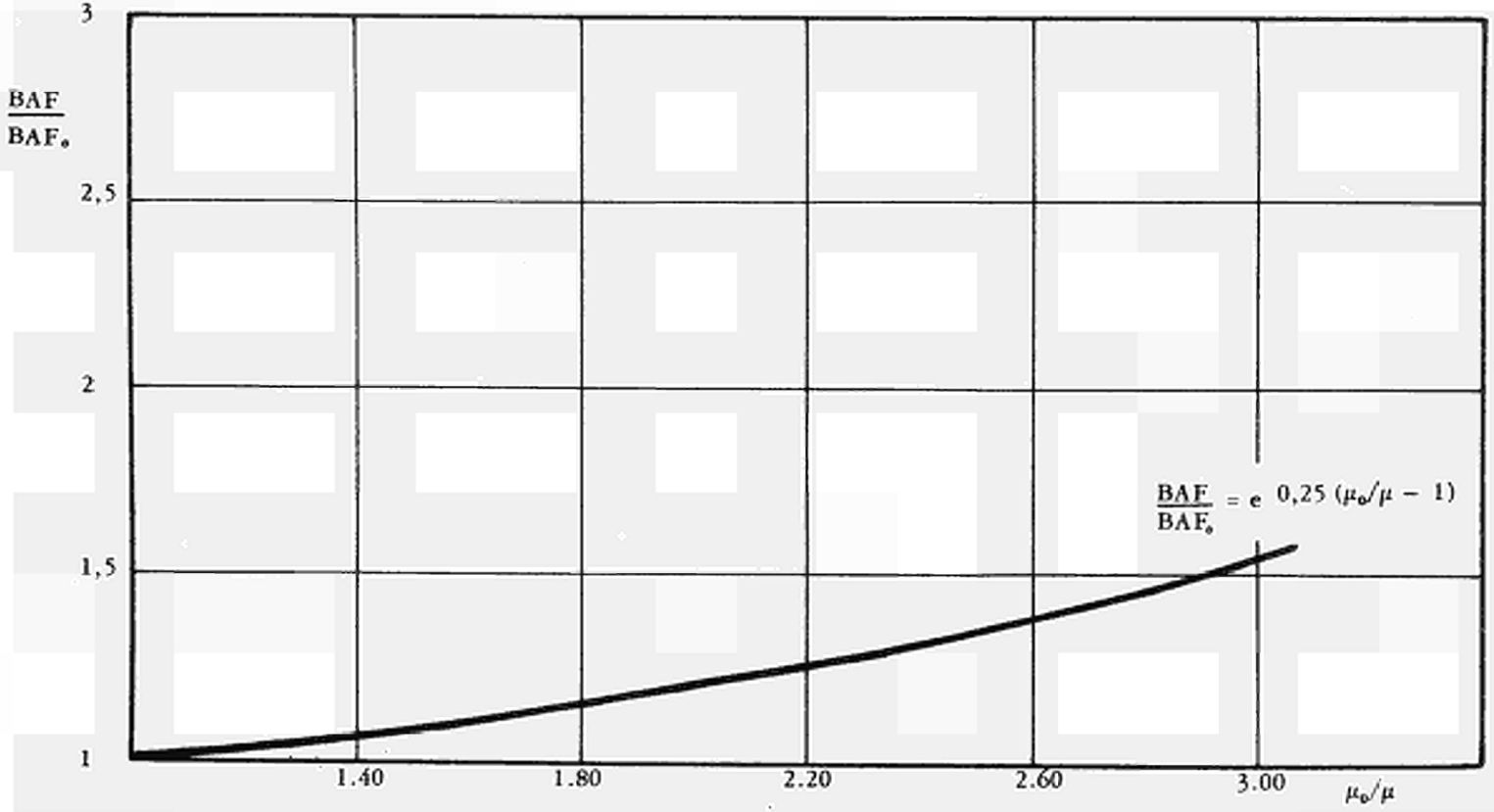


Fig. 4 Rate of increase of the Bacon anisotropy (B) depending on the decrease in the coating rate (μ/h) as a consequence of the continuous growth of the particle volume in the coater. (B_0 and μ_0 are respectively the Bacon anisotropy and the coating rate at the beginning of the coating cycle).

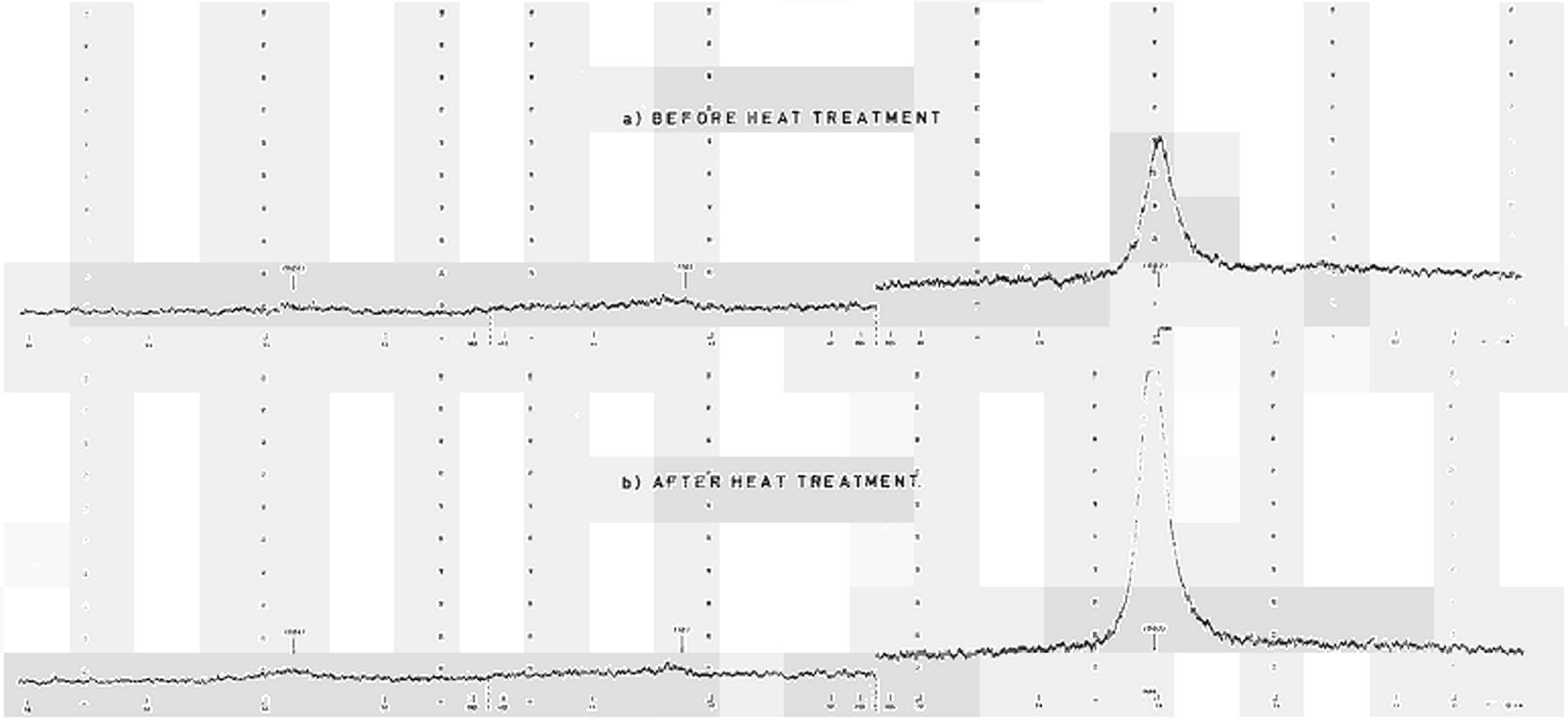


Fig. 5 Scattering diagrams of a 90 μ thick pyrocarbon disc deposited at 2000°C.
a) before heat treatment
b) after a heat treatment for 8 hours at 2000°C

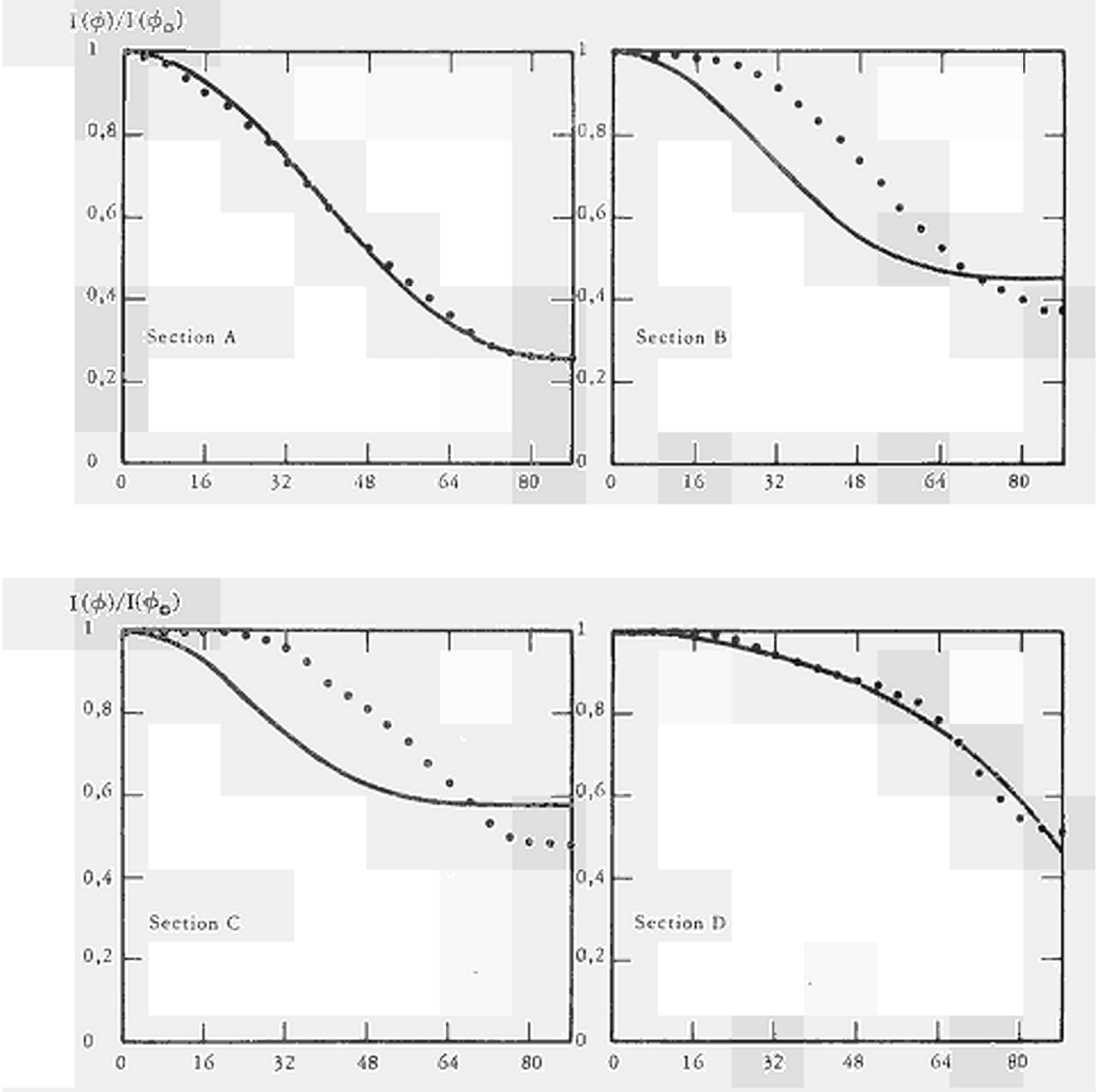


Fig. 6 Intensity distribution curves as obtained from different coating sections of sample WM 253

.... as measured

—— as calculated

- Fig. 7 -

WM 252: Deformation of 90 u thick coatings heat treated for 8 hours at 2000°C in a high frequency furnace and rapidly cooled down by switching off the furnace power.

- Fig. 8 -

WM 250: Deformation of 90 u thick coatings heat treated for 8 hours at 2000°C in a high frequency furnace and rapidly cooled down by switching off the furnace power.

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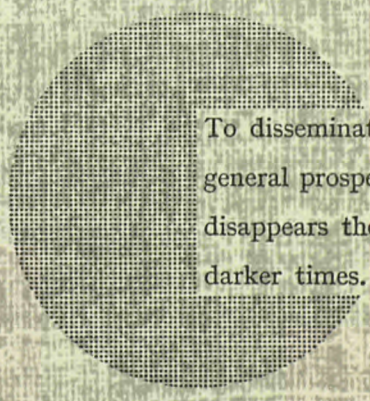

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Alfred Nobel

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